

AD-A041 489

STANFORD RESEARCH INST MENLO PARK CALIF MOLECULAR PH--ETC F/G 20/8
MEASUREMENT OF ION-ION NEUTRALIZATION REACTION RATES BY A MERGE--ETC(U)
MAY 77 J R PETERSON, T M MILLER, R E OLSON F44620-76-C-0018

UNCLASSIFIED

SRI-MP-77-41

AFOSR-TR-77-0714

NL

1 OF 12
AD
A041489



END

DATE
FILMED

7-77



STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.

AFOSR-TR- 77-0714

May 19, 1977

12

Final Report

MEASUREMENT OF ION-ION NEUTRALIZATION REACTION RATES
BY A MERGED BEAMS TECHNIQUE

by

James R. Peterson, Thomas M. Miller, and Ronald E. Olson

Contract F44620-76-C-0018
SRI Project 4561

Report No. MP 77-41

Prepared for

Air Force Office of Scientific Research
Bolling Air Force Base
Washington, D.C. 20332

Attn: Dr. Joseph Masi
Directorate of Aerospace Sciences



AD No. 041489
DDC FILE COPY

Approved for public release;
distribution unlimited.

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DDC
This technical report has been reviewed and is
approved for public release IAW AFR 190-12 (7b).
Distribution is unlimited.
A. D. BLOSE
Technical Information Officer

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

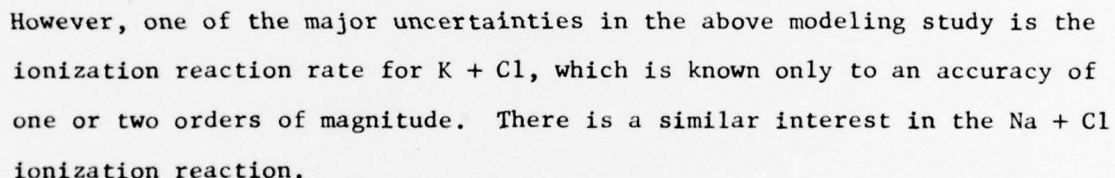
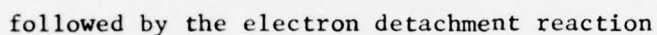
| 1. REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|-----------------------|---|
| 1. REPORT NUMBER | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 18 AFOSR-TR-77-0714 | | |
| 4. TITLE (and Subtitle) | | 5. TYPE OF REPORT & PERIOD COVERED |
| 6 MEASUREMENT OF ION-ION NEUTRALIZATION REACTION RATES BY A MERGED BEAMS TECHNIQUE. | | 7 FINAL Rept. 1 Sep 75 - 28 Feb 77 |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s) | | 8. CONTRACT OR GRANT NUMBER(s) |
| J. R. PETERSON (10) James R. Peterson T. M. MILLER Thomas M. Miller R. E. OLSON (15) Ronald E. Olson | | 15 F44620-76-C-0018 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS |
| STANFORD RESEARCH INSTITUTE MOLECULAR PHYSICS CENTER MENLO PARK, CALIFORNIA 94025 | | 16 9750-02 61102F (17) |
| 11. CONTROLLING OFFICE NAME AND ADDRESS | | 12. REPORT DATE |
| AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA BLDG 410 | | 11 19 May 1977 |
| BOLLING AIR FORCE BASE, D C 20332 | | 13. NUMBER OF PAGES |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | | 22 |
| 12 24p | | 15. SECURITY CLASS. (of this report) |
| | | UNCLASSIFIED |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |
| 16. DISTRIBUTION STATEMENT (of this Report) | | |
| Approved for public release; distribution unlimited. | | |
| 14 SRI-MP-77-41 | | |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) | | |
| 18. SUPPLEMENTARY NOTES | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) | | |
| ION PAIR FORMATION ION-ION RECOMBINATION CLOSE COUPLING CALCULATIONS Na + Cl AND K + Cl REACTIONS ROCKET EXHAUST PLUME IONIZATION | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) | | |
| <p>The forward and reverse cross sections have been calculated for Na + Cl (5) and K + Cl (5) using quantum close-coupling techniques with matrix elements derived from pseudo-potential calculations. The collision energy-dependent cross sections were Boltzmann-averaged to obtain temperature-dependent thermal reaction rate coefficients. At 1800°K the rate coefficients (cm³/sec) are k(Na⁺ + Cl⁻) = 4 x 10⁻¹⁰ and k(K⁺ + Cl⁻) = 0.9 x 10⁻¹⁰ for neutralization, and k(Na + Cl) = 1.7 x 10⁻¹⁴ and k(K + Cl) = 6.7 x 10⁻¹⁴ for ionization. The rates should be accurate to a factor of two or three, and are</p> | | |

409 198

thus probably more reliable than existing estimates. Equilibrium constants $k_{eq} = k_{recomb}/k_{ioniz}$ were also calculated for $1000^{\circ}K < T < 3000^{\circ}K$, yielding $k_{eq}(K-Cl) = 15.9 \exp(8180/T)$ and $k_{eq}(Na-Cl) = 15.4 \exp(17200/T)$. These values are 35% higher than the JANAF values. An effort was made to measure neutralization rates using an existing merged-beams apparatus. However, it proved impossible, within the limited scope of this contract, to obtain stable negative halogen beams of sufficient intensity to perform the measurements.

UNCLASSIFIED

There is considerable interest in determining the electrical properties of turbulent afterburning exhaust plumes of solid propellant rocket motors. Modeling calculations have been employed to calculate the radar interference effects that arise when communication with rockets involves transmission through these plumes. In a recent paper, Jensen and Pergament have shown that for systems where potassium is a major rocket exhaust impurity, above-equilibrium electron concentrations are principally formed by the chemi-ionization reaction



The particular reactions of importance for rocket plume processes have never been studied by beam techniques, although certain examples of the reverse reaction have been studied at the FOM Laboratory in Amsterdam. Our unique apparatus for studying ion-ion neutralization has previously made it possible for us to conduct an extensive set of measurements on the

of measurements on the

neutralization reactions of a considerable number of ion pairs of species containing H, O and N. Cross sections for fifteen ion pairs such as $H^+ + H^-$, $N^+ + O^-$, $O^+ + O^-$, $NO^+ + O^-$, $O_2^+ + O^-$, $N_2^+ + O_2^-$, $O_2^+ + O_2^-$, and $NO^+ + NO_2^-$ have been measured and rate constants determined. The work reported here was a small effort in which it was originally intended to use our existing beams equipment to extend our measurements of ion-ion neutralization cross sections to include alkali and halogen ion pairs. It was also intended to supplement this work by theoretical calculations, in order that the achievement of reasonable agreement between experiment and theory in the case of one or more alkali-halogen combinations would provide further confirmation of both approaches.

Unexpected experimental difficulties encountered in the course of the work have prevented a successful measurement within the limited scope of effort and funds originally allocated to this project. The difficulties have been identified, as have the modifications of the equipment and method that would be required for successful measurement.

The theoretical calculation has been successfully carried out employing significant improvements in computational technique and in parameters employed as compared to previous theoretical treatments of these reactions. In particular, close coupling calculations have been used instead of the simplified Landau-Zener formula. For the case of $K + Cl$, our current results differ from the Landau-Zener formula by several orders of magnitude.

EXPERIMENTAL

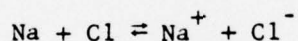
The experimental program was intended to take advantage of existing facilities with minimal modifications compatible with a small scale effort. For the initial neutralization measurements, we chose to work on the $Na^+ + F^-$ reaction because both atoms have only one stable isotope. An attempt to use isotopically mixed beams such as $^{35}Cl^- + ^{37}Cl^-$ would have led to experimental difficulties in focusing and beam deflection and would have

THEORETICAL CHEMI-IONIZATION AND RECOMBINATION
CROSS SECTIONS FOR REACTIONS OF Na AND K WITH Cl

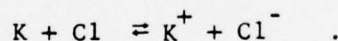
R. E. Olson^{*}
Molecular Physics Center, Stanford Research Institute,
Menlo Park, California 94025

ABSTRACT

Quantum close-coupling techniques employing pseudo-potential derived coupling matrix elements between reactant and product states have been used to calculate the cross sections for the reactions



and



The calculations were performed from threshold collision energies to 5.0 eV, allowing the reaction rates to be determined for temperatures $T \leq 5000^\circ\text{K}$. Analytical forms for the reaction rates are given. Representative reaction rates at 2000°K for the ionization reactions are $k(\text{Na} + \text{Cl}) = 4.3 \times 10^{-14} \text{ cm}^3/\text{sec}$ and $k(\text{K} + \text{Cl}) = 1.0 \times 10^{-13} \text{ cm}^3/\text{sec}$, while for the ion-ion recombination reactions the rates are found to be $k(\text{Na}^+ + \text{Cl}^-) = 3.7 \times 10^{-9} \text{ cm}^3/\text{sec}$ and $k(\text{K}^+ + \text{Cl}^-) = 8.5 \times 10^{-11} \text{ cm}^3/\text{sec}$. It is believed that the calculated rates are accurate to within a factor of two or three.

INTRODUCTION

There is considerable interest in determining the electrical properties of turbulent afterburning exhaust plumes of solid propellant rocket motors. Modeling calculations have been employed to calculate the radar interference effects that arise when communication with rockets involves transmission through these plumes. In a recent paper, Jensen and Pergament¹ have shown that for systems where potassium is a major rocket exhaust impurity, above-equilibrium electron concentrations are principally formed by the chemi-ionization reaction

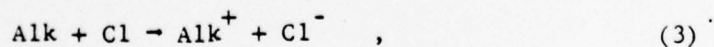


followed by the electron detachment reaction

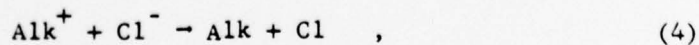


However, one of the major uncertainties in the above modeling study is the ionization reaction rate for $K + Cl$, which is known only to an accuracy of one or two orders of magnitude. There is a similar interest in the $Na + Cl$ ionization reaction.

In this paper, we address ourselves to the problem of calculating the cross sections for the ionization reaction



and the recombination reaction



where Alk represents Na or K. The reason for including the recombination reaction (4) in the calculations is that experimental data² exist for 1800°K which can be used to test the theoretical approach. The recombination cross sections are obtained along with the ionization cross sections in the same calculation.

For the theoretical cross section determinations, we have employed the quantum close-coupling method³ and coupling matrix elements obtained from pseudo-potential calculations⁴ to obtain the transition probabilities for reaction. The cross sections are then derived from the calculated transition probabilities and the reaction rates are obtained by averaging the cross sections over a Maxwellian distribution of collision velocities. When possible we compare the theoretical reaction rates to existing experimental data.

THEORETICAL APPROACH

The calculation of the cross sections for Reactions (3) and (4) are extremely amenable to theoretical attack since we need only consider three reactant and product channels. These are the $\text{Alk}^+ + \text{Cl}^-$ ionic channel and two neutral states arising from the interaction of the ground state alkaline atom and chlorine in its two lowest fine structure states: $^2P_{3/2}$ and $^2P_{1/2}$. Higher lying excited states of the neutral alkali-chlorine atom lie above the asymptotic energy of the positive ion (Alk^+)-negative ion (Cl^-) pair and hence to first order do not interact with the attractive coulomb potential of $\text{Alk}^+ + \text{Cl}^-$. The collision mechanism is primarily a curve

crossing transition induced in the regions of the curve crossings between the long-range attractive coulomb potential $(-1/R)$ of the ion pair $\text{Alk}^+ + \text{Cl}^-$ and the covalent potentials $(-C_{ab}/R^6)$ of the neutral species. At the large internuclear distance where the curve crossing occurs, the covalent potentials of the neutral species are essentially constant and may be accurately replaced by their asymptotic dissociation energies. The curve crossing distances for the two systems are given in Table I.

The quantum close-coupling technique for obtaining the transition probabilities as a function of impact parameter b and collision energy E has been described many times previously.^{3,5} The input parameters for the close-coupling calculations are: (a) the internal energy change ΔE for the reaction; we have used the spectroscopic levels from volume I of Charlotte Moore;⁶ (b) the initial and final state potentials; the potentials described in the previous paragraph have been modified to include a repulsive wall so that there would be no unphysical trapping of the particles by a purely attractive coulomb potential; and (c) the coupling between the two channels. In the close-coupling calculations it is necessary to include the R dependence of the coupling matrix element. We have therefore used the functional form described previously⁷ with a modification of the pre-exponential coefficient so that we could reproduce the coupling at the crossing point to obtain the pseudo-potential values of $H_{12}(R_x)$. For the Na-Cl systems, the form is given by

$$H_{12}(R) = 8.98 \alpha R \exp(-1.064 R) \quad , \quad (5a)$$

while for K-Cl we used

$$H_{12}(R) = 7.89 \alpha R \exp(-1.017 R) \quad . \quad (5b)$$

In Eqs. (5), the internuclear separation R is given in units of $\overset{0}{A}$ while the energy is in units of electron-volts. Since the pseudo-potential calculations did not incorporate the fine structure states of Cl, it is necessary to include in the matrix elements a factor α which is $(\frac{2}{3})^{\frac{1}{2}}$ for the $\text{Alk} + \text{Cl}(^2P_{\frac{3}{2}})$ state and $(\frac{1}{3})^{\frac{1}{2}}$ for the $\text{Alk} + \text{Cl}(^2P_{\frac{1}{2}})$ state.

The output of the close-coupling calculation is the transition probability for reaction $P(b)$ vs the impact parameter b . The total cross section for a given collision energy is then given by the integral

$$Q = 2\pi S \int_0^{\infty} db \cdot b \cdot P(b) \quad , \quad (6)$$

where S is the statistical weight factor for the reaction. For the ionization reactions, we have employed j-j notation for the molecular states formed during the collision and find that the appropriate statistical weight S to be used for ionization from the $\text{Alk} + \text{Cl}(^2P_{\frac{3}{2}})$ state is $1/8$, while from the $\text{Alk} + \text{Cl}(^2P_{\frac{1}{2}})$ state it is $1/4$. For the reverse reactions, that of ion-ion recombination, the statistical weight factor is unity.

We may average the cross sections over a Maxwellian distribution of collision velocities in order to calculate the reaction rates:

$$k = \frac{8\pi\mu}{(2\pi\mu kT)^{\frac{3}{2}}} \int_0^{\infty} dE \cdot E \cdot Q(E) \cdot \exp(-E/kT) \quad (7)$$

Moreover, since the recombination cross sections at low collision energies are proportional to $1/E$,⁸ a formula for the low temperature reaction rate may be derived from Eq. (7) that varies as $T^{-\frac{1}{2}}$:

$$k = \frac{4[E \cdot Q(E)]}{(\pi\mu kT)^{\frac{1}{2}}} \quad (8)$$

It is also possible to calculate the cross sections for Reactions (3) and (4) by using the Landau-Zener method. However, this method cannot be expected to yield cross sections with an accuracy greater than a factor of two even when the coupling terms are known exactly.^{9,10} Furthermore, for a curve crossing at a large internuclear separation, such as in the K-Cl system, the Landau-Zener method may greatly underestimate the cross section due to the neglect of the coupling over an extended region near the curve crossing where the potential energy curves are still close together.

RESULTS AND DISCUSSION

The calculated ionization cross sections for reactions (3) are given in Table II. At collision energies just above threshold, the cross sections are almost constant. This behavior is expected since the collision velocity which induces the transitions and determines the transition probabilities is varying only slightly in the threshold region, and because the maximum impact parameter collision that contributes to the cross section, Eq. (6), is also approximately constant. We should reiterate that the ionization cross sections given in Table II include the $1/8$ statistical weight factor

for $\text{Alk} + \text{Cl}(^2P_{3/2})$ collisions and a 1/4 statistical weight factor for $\text{Alk} + \text{Cl}(^2P_{1/2})$ collisions.

The ion-ion recombination cross sections for Reactions (4) are presented in Table III. As expected,¹⁰ the low energy cross sections, which are dominated by the strongly attractive coulomb potential, decrease as $1/E$ yielding a low temperature reaction rate, Eq. (8), that is proportional to $T^{-1/2}$.

The ionization and recombination cross sections given in Tables II and III may be used to calculate the reaction rates by employing Eq. (7). For the ionization reactions, two rates are obtained for each system that correspond to ionization from the $\text{Alk} + \text{Cl}(^2P_{3/2})$ and $\text{Alk} + \text{Cl}(^2P_{1/2})$ fine structure states. For low temperature reactions, $T \leq 1000^\circ\text{K}$, the reactant Cl will be preferentially in its ground $^2P_{3/2}$ state so that the rate given for $\text{Alk} + \text{Cl}(^2P_{3/2})$ will apply. However, at higher temperatures, the fine structure states of Cl will most likely be populated statistically with $\frac{2}{3}$ in the $\text{Cl}(^2P_{3/2})$ state and $\frac{1}{3}$ in the $\text{Cl}(^2P_{1/2})$ state, so that a weighted combination of the rates given should be used.

For $\text{K} + \text{Cl}$ ionization, we find the following reaction rates:

$$k[\text{K} + \text{Cl}(^2P_{3/2})] = 2.2 \times 10^{-14} T^{1/2} (1 + 8400/T) \exp(-8400/T) \quad (9a)$$

and

$$k[\text{K} + \text{Cl}(^2P_{1/2})] = 2.6 \times 10^{-14} T^{1/2} (1 + 7140/T) \exp(-7140/T) \quad (9b)$$

Likewise, for ionization of $\text{Na} + \text{Cl}$, the rates are found to be

$$k[\text{Na} + \text{Cl}(^2\text{P}_{3/2})] = 6.2 \times 10^{-13} T^{\frac{1}{2}} (1 + 17700/T) \exp(-17700/T) \quad (10a)$$

and

$$k[\text{Na} + \text{Cl}(^2\text{P}_{1/2})] = 4.3 \times 10^{-13} T^{\frac{1}{2}} (1 + 16400/T) \exp(-16400/T) \quad (10b)$$

In Eqs. (9) and (10), the reaction rates k are in units of cm^3/sec , while the temperature T is in $^{\circ}\text{K}$ and the exponential constants are the thermodynamic endoergicities. The temperature range of validity for the rates is $T \leq 5000^{\circ}\text{K}$.

The ion-ion recombination rates are calculated to be

$$k(\text{K}^+ + \text{Cl}^-) = 3.1 \times 10^{-9} T^{-\frac{1}{2}} (1 + 2.6 \times 10^{-6} T^{\frac{3}{2}}) \quad (11a)$$

and

$$k(\text{Na}^+ + \text{Cl}^-) = 1.6 \times 10^{-7} T^{-\frac{1}{2}} (1 + 4.7 \times 10^{-7} T^{\frac{3}{2}}) \quad (11b)$$

The units are the same as those given for the ionization rates. In Eqs. (11), the rates are predominately a function of $T^{-\frac{1}{2}}$ with a small correction factor for the higher temperatures.

We may compare the calculated reaction rates to two sets of experimental measurements. For ion-ion recombination, Hayhurst and Sugden² have indirectly measured the reaction rates for Reactions (4) at 1800°K . For $\text{Na}^+ + \text{Cl}^-$ recombination, the experimentally derived rate is $6 \times 10^{-10} \text{ cm}^3/\text{sec}$, while the theoretical value is $3.9 \times 10^{-9} \text{ cm}^3/\text{sec}$. For $\text{K}^+ + \text{Cl}^-$ recombination there is a smaller difference: the experimental value is $1.6 \times 10^{-10} \text{ cm}^3/\text{sec}$ while the theoretical rate is $8.8 \times 10^{-11} \text{ cm}^3/\text{sec}$. The uncertainties in the experimental rates have been estimated by Jensen and Jones¹¹ to be approximately a factor of 5. Moreover, since we expect the theoretical

values to be accurate to only a factor of two or three, we can conclude that the theoretical recombination rates are in reasonable agreement with experiment.

No direct measurement of the ionization reaction rates exists; however, a rough value for $K + Cl$ ionization has been inferred from the modeling of the transverse radar attenuation in a rocket plume. At $T \approx 1600^\circ K$, Jensen and Pergament¹ have used a value of $k(K + Cl) = 1.3 \times 10^{-13} \text{ cm}^3/\text{sec}$ and conclude that this value is too large by approximately an order of magnitude. In comparison, the theoretical value at $1600^\circ K$ for a statistical population of the Cl fine structure states is $4.1 \times 10^{-14} \text{ cm}^3/\text{sec}$. Hence, the theoretical rate is smaller than the original $K + Cl$ ionization rate used by Jensen and Pergament, and is in the direction to more accurately reproduce the radar attenuation data. However, our rate is still a factor of 3.2 greater than their best estimate for this reaction rate.

We have also used a statistical combination of the ionization reaction rates along with the ion-ion recombination rates to estimate the equilibrium constant, k_{eq} , where

$$k_{eq} = k_{recomb} / k_{ionization} \quad (12)$$

The theoretical equilibrium constant for $K-Cl$ in the temperature range $1000^\circ K \leq T \leq 3000^\circ K$ is found to be

$$k_{eq}^{theory} (K - Cl) = 15.9 \exp (8180/T) \quad (13)$$

This expression may be compared to that given in the JANAF tables:¹²

$$k_{eq}^{JANAF} (K - Cl) = 11.4 \exp (8200/T) . \quad (14)$$

The theoretical equilibrium constant is approximately 35% larger than the form given in the JANAF tables. Similarly, for the Na - Cl reactions we obtain

$$k_{eq}^{theory} (Na - Cl) = 15.6 \exp (17200/T) , \quad (15)$$

while this expression may be compared to

$$k_{eq}^{JANAF} (Na - Cl) = 11.3 \exp (17480/T) . \quad (16)$$

In the temperature range of 1000 to 3000^oK, equilibrium values obtained from Eqs. (15) and (16) agree to within 25%. In both Eqs. (13) and (15), the constants were obtained from a curve fit to the temperature dependence of the theoretical equilibrium values.

We have also used the Landau-Zener (LZ) method⁹ to estimate the ionization cross sections for the Na + Cl and K + Cl reactions. For Na + Cl, the LZ cross sections are in reasonable agreement and are ~ 40% lower than the close-coupling results. However, for K + Cl, the LZ cross sections are several orders of magnitude below the close-coupling results. The reason is that the LZ method only allows transitions at the crossing point. Thus, for a case with a distant crossing such as K + Cl, the transition probabilities are greatly underestimated since strong coupling can occur over an extended region on either side of the curve crossing where the potential energy curves lie close together. A similar conclusion has been arrived at by Weiner et al.¹³ in the analysis of their experimental data on the Na⁺ + O⁻ reaction.

The calculated transition probabilities, $P(b)$, have a regular oscillatory structure as a function of impact parameter which is associated with a curve crossing process.¹⁴ For both the Na-Cl and K-Cl systems, the magnitude of $P(b)$ are largest at small impact parameters and rapidly decrease to zero for impact parameters whose classical turning points are outside the crossing distance. We can obtain an estimate of the average transition probability for a specific collision energy by using the ionization cross sections given in Table II and the formula

$$\overline{P(b)} = Q_{\text{ION}} \div \pi R_x^2 . \quad (17)$$

If we are concerned with the transition probability for scattering only on the ground state, then the $\overline{P(b)}$ calculated from Eq. (17) must be divided by the statistical weight factor S which is $1/8$ for $\text{AlK} + \text{Cl}(^2P_{3/2})$ collisions and $1/4$ for $\text{AlK} + \text{Cl}(^2P_{1/2})$ collisions. Representative values of $\overline{P(b)}$ for scattering on the ground state are 1-5% for the Na-Cl system and 0.01-0.1% for the K-Cl system.

Probably of greater interest is an estimate of the branching ratio between neutral and ionic products in the collisional dissociation of NaCl and KCl molecules. For this problem we only want the transition probability, p , for a single passage of the crossing points. A good approximation is to use the Landau-Zener formula to solve for p :

$$P = 2p(1-p) . \quad (18)$$

For the Na-Cl and K-Cl systems, the transition probabilities are small so we may set $p = P/2$.

It is more difficult to make an estimate of the branching ratio for a Boltzmann distribution of gas whose mean temperature is less than the

endoergicity of the reaction. We may, however, use the rates given by Eqs. (9) and (10) and divide by the mean velocity to obtain a cross section for use in Eq. (17). Such a calculation was performed for Na-Cl and we find the theoretical branching ratio of neutral to ionic products is within a factor of three to the branching ratio measured by Ewing et al.¹⁵ We also substantiate their observation of a large temperature dependence of the branching ratio for NaCl collisional dissociation and find the neutral to ionic ratio decreasing by a factor of 50 between 6400°K and 3000°K. For the KCl system we also concur with the findings of Ewing et al.¹⁵ that the collisional dissociation primarily produces ionic products and find theoretical branching ratios that are approximately two orders of magnitude smaller than for NaCl.

SUMMARY

The theoretical reaction rates given by Eqs. (9), (10) and (11) should be accurate to a factor of two or three since the potential energy curves and coupling matrix elements are known to a sufficient accuracy. Moreover, we would not expect rotational coupling (we have only considered radial coupling) to be important in inducing transitions since the collision velocities are quite low.

This work was originally started to meet the need for more accurate values for the ionization reaction rates for K - Cl and Na - Cl collisions. It is hoped that the reaction rates and their temperature dependencies given by Eqs. (9) and (10) will be an aid to future rocket plume modeling studies.

Very recently, theoretical calculations have been performed by Arora et al.¹⁶ for the K - Cl and Na - Cl ionization cross sections. High energy approximations were used to estimate these cross sections for collision energies $E \geq 500$ eV. However, the low energy velocity dependence and magnitude of the cross sections predicted by these authors is in disagreement with the results given here. Moreover, extrapolation of their results to thermal energies would yield ionization cross sections on the order of 10^{-20} cm^2 and predict reaction rates substantially smaller than the experimental determinations.

ACKNOWLEDGEMENTS

The author would like to thank Drs. D. L. Huestis and J. R. Peterson for their helpful discussions.

REFERENCES

*Work supported by the Air Force Office of Scientific Research under Contract No. F44620-76-C-0018.

1. Jensen, D. E. and Pergament, H. S., Combust. Flame 17, 115-124 (1971).
2. Hayhurst, A. N. and Sugden, T. M., Trans. Faraday Soc. 63, 1375-1384 (1967).
3. Evans, S. A., Cohen, J. S., and Lane, N. F., Phys. Rev. A 4, 2235-2248 (1971).
4. Grice, R., and Herschbach, D. R., Mol. Phys. 27, 159-175 (1974).
5. Olson, R. E., and Smith, F. T., Phys. Rev. A 3, 1607-1617 (1971).
6. Moore, C. E., Atomic Energy Levels, NBS Circular 467, U.S. Government Printing Office, WDC, 1949, Vol. I.
7. Olson, R. E., Smith, F. T., and Bauer, E., Appl. Optics, 10, 1848-1855 (1971).
8. Moseley, J. T., Olson, R. E., and Peterson, J. R., in Case Studies in Atomic Physics (M.R.C. McDowell and E. W. McDaniel, Eds.) North-Holland Publishing, Amsterdam, Vol. 5, p. 18.
9. Olson, R. E., Peterson, J. R., and Moseley, J., J. Chem. Phys. 53, 3391-3397 (1970).
10. Olson, R. E., J. Chem. Phys. 56, 2979-2984 (1972).
11. Jensen, D.E., and Jones, G. A., Rocket Propulsion Establishment Report No. 71/9, October 1971.
12. JANAF Thermochemical Tables, Ed. by H. Prophet (Dow Chemical Co., Midland, Mich., revised version, June 1971).

13. Weiner, J., Peatman, W. B., and Berry, R. S., Phys. Rev. A 4,
1824-1835 (1971).
14. Olson, R. E., and Smith, F. T., Phys. Rev. A 3, 1607-1617 (1974).
15. Ewing, J. J., Milstein, R., and Berry, R. S., J. Chem. Phys. 54,
1752-1760 (1971).
16. Arora, D., Turner, J. E., and Khubchandani, P. G., Phys. Rev. A 14,
2089-2094 (1976).

Table I

CURVE CROSSING PARAMETERS

| <u>System</u> | <u>$R_x - \overset{0}{A}$</u> | <u>$\Delta E - eV$</u> |
|------------------------|--|-----------------------------------|
| K + Cl($^2P_{3/2}$) | 19.9 | 0.724 |
| K + Cl($^2P_{1/2}$) | 23.4 | 0.615 |
| Na + Cl($^2P_{3/2}$) | 9.5 | 1.523 |
| Na + Cl($^2P_{1/2}$) | 10.2 | 1.414 |

Table II

IONIZATION CROSS SECTIONS VERSUS COLLISION ENERGY

| System | E - eV | $Q_{\text{ion}} - \text{cm}^2$ |
|------------------------|--------|--------------------------------|
| K + Cl($^2P_{3/2}$) | 0.734 | $6.1(-18)^*$ |
| | 0.749 | $6.1(-18)$ |
| | 0.774 | $5.6(-18)$ |
| | 0.824 | $5.9(-18)$ |
| | 0.974 | $6.9(-18)$ |
| | 1.224 | $8.3(-18)$ |
| | 1.724 | $1.1(-17)$ |
| | 3.224 | $1.5(-17)$ |
| | 5.724 | $1.8(-17)$ |
| K + Cl($^2P_{1/2}$) | 0.625 | $7.8(-18)$ |
| | 0.640 | $9.1(-18)$ |
| | 0.665 | $8.0(-18)$ |
| | 0.715 | $7.5(-18)$ |
| | 0.865 | $7.9(-18)$ |
| | 1.115 | $9.5(-18)$ |
| | 1.615 | $1.1(-17)$ |
| | 3.115 | $1.4(-17)$ |
| Na + Cl($^2P_{3/2}$) | 5.615 | $1.6(-17)$ |
| | 1.533 | $1.4(-16)$ |
| | 1.548 | $1.7(-16)$ |
| | 1.573 | $1.7(-16)$ |
| | 1.623 | $1.4(-16)$ |
| | 1.773 | $1.6(-16)$ |
| | 2.023 | $1.6(-16)$ |
| | 2.523 | $1.2(-16)$ |
| Na + Cl($^2P_{1/2}$) | 4.023 | $1.1(-16)$ |
| | 6.523 | $9.9(-17)$ |
| | 1.424 | $9.7(-17)$ |
| | 1.439 | $7.3(-17)$ |
| | 1.464 | $6.6(-17)$ |
| | 1.514 | $7.3(-17)$ |
| | 1.664 | $7.2(-17)$ |
| | 1.914 | $6.1(-17)$ |
| | 2.414 | $6.5(-17)$ |
| | 3.914 | $5.8(-17)$ |
| | 6.414 | $5.7(-17)$ |

* $6.1(-18)$ means 6.1×10^{-18} .

Table III

ION-ION RECOMBINATION CROSS SECTIONS VERSUS COLLISION ENERGY

| System | E-eV | $Q_{\text{recomb}} \text{-cm}^2$ | $EQ\text{-eV cm}^2$ |
|-----------------------------|-------|----------------------------------|---------------------|
| $\text{K}^+ + \text{Cl}^-$ | 0.010 | $5.5(-15)^*$ | $5.5(-17)$ |
| | 0.025 | $2.2(-15)$ | $5.6(-17)$ |
| | 0.050 | $1.1(-15)$ | $5.6(-17)$ |
| | 0.10 | $6.0(-16)$ | $6.0(-17)$ |
| | 0.25 | $3.2(-16)$ | $8.1(-17)$ |
| | 0.50 | $2.5(-16)$ | $1.2(-16)$ |
| | 1.0 | $2.2(-16)$ | $2.2(-16)$ |
| | 2.5 | $2.2(-16)$ | $5.6(-16)$ |
| | 5.0 | $2.4(-16)$ | $1.2(-15)$ |
| $\text{Na}^+ + \text{Cl}^-$ | 0.010 | $2.5(-13)$ | $2.5(-15)$ |
| | 0.025 | $9.9(-14)$ | $2.5(-15)$ |
| | 0.050 | $4.9(-14)$ | $2.5(-15)$ |
| | 0.10 | $2.6(-14)$ | $2.6(-15)$ |
| | 0.25 | $1.1(-14)$ | $2.7(-15)$ |
| | 0.50 | $6.0(-15)$ | $3.0(-15)$ |
| | 1.0 | $3.1(-15)$ | $3.1(-15)$ |
| | 2.5 | $1.8(-15)$ | $4.6(-15)$ |
| | 5.0 | $1.3(-15)$ | $6.6(-15)$ |

* $5.5(-15)$ means 5.5×10^{-15} .